



IN THE UNITED STATES PATENT AND TRADEMARK

In re the Application of:

Patrick Leempoel, et al

Serial Number: 10/008282

Filed: November 7, 2001

Title: PROCESS FOR THE MANUFACTURE OF ORGANOPOLYSILOXANE COMPOSITIONS

Attorney Docket: SN - 116

) Group Art Unit:

) Examiner:

) Submission of
) Certified Copy

) December 19, 2001

1621
tly
Mw
RECEIVED
JAN 25 2002
TECH CENTER 1600/2900

Assistant Commissioner
for Patents
Washington DC 20231

Dear Sir:

Applicant hereby encloses a certified copy of the above-identified patent application, namely, United Kingdom, filed November 21, 2000 as 0028254.1 in the name of Dow Corning S.A.

Respectfully submitted,

Robert L. McKellar
Reg. No. 26,002
(989) 631-4551



INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

RECEIVED
JAN 25 2002
TECH CENTER 1600/2900

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

Dated 6 November 2001

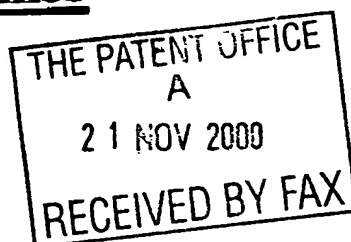
21NOV00 E585159-1 002914
F01/7700 0.00-0028254.1

Patents Form 1/77

Patents Act 1977
(Rule 16)The
Patent
Office

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)



The Patent Office

Cardiff Road
Newport
South Wales
NP9 1RH

1. Your reference

SN116

2. Patent application number

(The Patent Office will fill in this part)

0028254.1

3. Full name, address and postcode of the or of each applicant (underline all surnames)

DOW CORNING S.A.
Parc Industriel
B-7180 Seneffe
Belgium
5806740001 ✓

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

Belgium

1. Title of the invention

ORGANOPOLYSILOXANE COMPOSITIONS AND THEIR PREPARATION

5. Name of your agent (if you have one)

A M Donlan

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

DOW CORNING LIMITED
Intellectual Property Department
Cardiff Road
Barry
CF63 2YL

Patents ADP number (if you know it)

7995244002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

Yes

Patents Form 1/77

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form.
Do not count copies of the same document

Continuation sheets of this form

Description 25

Claim(s) 5

Abstract

Drawing(s) 2

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

1

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

1 Fee Sheet

11.

I/We request the grant of a patent on the basis of this application.

Signature

A M Donlan

Date

21 November 2000

12. Name and daytime telephone number of person to contact in the United Kingdom

A M Donlan 01446 723740

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

DUPLICATE

- 1 -

ORGANOPOLYSILOXANE COMPOSITIONS AND THEIR PREPARATION

[0001] The present invention relates to organopolysiloxane compositions and in particular to a method of producing such compositions.

[0002] Organopolysiloxane compositions which cure to elastomeric solids are well known. Typically such compositions are obtained by mixing a polydiorganosiloxane having reactive terminal groups, generally silanol groups, with an organosilane cross-linking agent for the polydiorganosiloxane, for example an alkoxy silane, an acetoxysilane, an oximo silane, alkenyloxy silane or an amino silane. These materials are frequently curable upon exposure to atmospheric moisture at room temperature.

[0003] One important application of the above-described curable compositions is their use as sealants in which there is formed an elastomeric mass between surfaces which is adherent to at least two such surfaces. One important requirement of such materials is the ability to adhere well to a variety of substrates and it is a normal practice to include so called adhesion promoters in such compositions. The use of plastics in various industries, particularly the construction industry, is increasing. This is especially true for plastics such as polyvinyl chloride (PVC), used for window frames, polymethylmethacrylate (PMMA), used for bathtub and bathroom accessories, and polycarbonate (PC) such as Lexan, used as transparent sheeting material or for the manufacture of safety glass laminates and insulating glass units. Other substrates to which the sealant is expected to adhere are, for example, polyvinylidene fluoride or polyesters which tend to be used to coat metal surfaces.

[0004] Fillers used in these compositions may be divided into two types, reinforcing fillers and extending fillers.

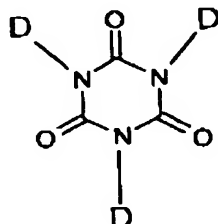
- 2 -

Reinforcing fillers are typically surface active in that they contain reactive groups on their outer surface which may react with other components in organopolysiloxane compositions. Examples of reinforcing fillers include fumed silica, calcined silica, precipitated silica, titania, zinc oxide, clay and mica all of which are used for the purpose of imparting mechanical strength to the cured products. The reinforcing fillers may be surface treated with hydrophobing agents such as organochlorosilane, organopolysiloxane, or hexamethyldisilazane prior to use but whilst such surface treated silicas "give" good plastic adhesion they are expensive and cause negative rheological effects to resulting sealant compositions. Extending fillers include ground calcium carbonate, magnesium carbonate, quartz, diatomaceous earth, barium sulphate, and calcium sulphate. It is also to be noted that some fillers such as precipitated calcium carbonate can be considered as semi-reinforcing in that they provide compositions with a degree of reinforcement.

[0005] Whilst many sealants containing extending fillers such as calcium carbonate are known to develop sufficient adhesion to the plastics discussed above, silica filled materials typically show poorer plastic adhesion properties. It is known to include adhesion promoters in sealant compositions using alkoxy silane cross-linkers, for example, alkoxy-silanes such as aminoalkylalkoxy silane, epoxyalkylalkoxy silane, mercaptoalkylalkoxy silane, or derivatives thereof, to ensure adhesion to plastics, particularly to PVC, PMMA and PC. However, we have found that usually with silica filled alkoxy compositions, the presence of such silanes is not sufficient to provide reliable adhesion on plastics. Another group of compounds which have been used as adhesion promoters for some

- 3 -

considerable time are silicon containing isocyanurates as described in, for example US3517001, US3708467 and US4100129. Typically these comprise:-



5

wherein one D substituent is $-R_y-Si-(R''_x)(OR''_{3-x})$, in which R is a divalent hydrocarbon radical selected from alkylenearylene, alkylene, cycloalkylene and halo substituted derivatives thereof, R'' is an alkyl or haloalkyl radical with up to 8 carbon atoms, x is from 0 to 3 and y is 1. The remaining D substituents being selected from $-R_y-Si-(R''_x)(OR''_{3-x})$ as described above, styryl, vinyl, allyl, chloroallyl or cyclohexenyl.

15 [0006] US3517001 describes the preparation of a variety of silicon containing isocyanurates of the type indicated above and indicates their use as adhesion promoters with silicone compositions. US3708467 and US4100129 both describe sealant compositions containing a silanol-terminated
20 polydiorganosiloxane, a silane cross-linking agent, a titanate catalyst and optionally fillers such as silicas and isocyanurate adhesion promoters. Preferred uses for such compositions including being sealants and caulking compounds.

25 [0007] The preferred process for making such sealants in the presence of an adhesion promoter is combining all the ingredients other than the silane cross-linker, the titanate catalyst and the adhesion promoter to form a base blend, removing moisture and adding the silane cross-linker,

- 4 -

titanate catalyst and adhesion promoter just prior to packaging the resulting composition. US4102852 describes a one component self extinguishing cured silicone composition using dimethyl and phenyl-methyl hydroxy polysiloxane polymers in combination with a selection of reinforcing and extending fillers as well as carbon black. The catalyst is a dialkoxo chelated titanium and an adhesion promoter, preferably 1,3,5-tris (trimethoxysilylpropyl) isocyanurate, may be used. The composition is prepared by mixing all the ingredients in any order desired, however a preferred process consists of adding the carbon black and then the other fillers into the polymer, then the cross-linker and finally the titanate catalyst "and/or any additional optional additives are mixed into the composition". It is indicated that a drying cycle must occur prior to the addition of the cross-linker and catalyst. In the examples, the adhesion promoter is added via a premix made of the catalyst, cross-linker and adhesion promoter so that all the silanes and the titanate catalyst are added in 1 step at the end of the manufacturing process.

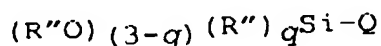
[0008] The above process may be appropriate in certain circumstances but it is often found that such a method can lead to a poor sealant rheology and slumping particularly if the catalyst and cross-linker are added into the reaction mixture after the addition of the filler.

[0009] The inventors have identified an improved process for the preparation of an organopolysiloxane composition suitable for use as a sealant which provides a resulting sealant with significantly improved adhesive properties.

[0010] According to a first aspect of the invention, there is provided a process for making an organopolysiloxane composition comprising mixing the following components

- 5 -

- i) a polymer having not less than two groups bonded to silicon which are hydroxyl or hydrolysable groups or a partial condensate thereof,
- ii) a surface active filler selected from silica, titania, zinc oxide, clay, mica and precipitated calcium carbonate
- iii) an organosilane comprising at least two silicon bonded reactive groups which are reactable with said surface active filler
- iv) a catalyst and
- v) an adhesion promoter having at least one hydrolysable group, having the formula



wherein R'' is as defined above, Q is a saturated, unsaturated or aromatic hydrocarbon radical functionalised by a group selected from amino, mercapto, ether, epoxy, isocyanato, cyano, isocyanurate acryloxy and acyloxy and mixtures thereof and q is 0 to 3

characterised in that organosilane (iii) is mixed with surface active filler (ii) to form an in-situ modified surface active filler prior to the introduction of the adhesion promoter.

[0011] It is to be understood that the concept "comprising" where used herein is used in its widest sense to mean and to encompass the notions of "include", "comprehend" and "consist of".

[0012] The polymer is according to the general formula W-B-W where B may be any desired organic or siloxane molecular chain for example a polyoxyalkylene chain, a polyisobutylene chain or more preferably a polydiorganosiloxane chain and

- 6 -

thus preferably includes siloxane units of the formula $R^2_5SiO(4-s)/2$ in which R^2 represents an alkyl group, having from 1 to 6 carbon atoms, for example a methyl group, a vinyl group having from 1 to 6 carbon atoms a phenyl group, or a halo-substituted alkyl group, preferred halogen substituents being chlorine or fluorine and s has a value of 0, 1 or 2. Preferred materials are linear materials i.e. $s = 2$ for all units, thereby having polydiorganosiloxane chains according to the general formula $-(R^2_2SiO)_t-$ in which each R^2 represents a methyl group or ethyl group and t has a value from about 200 to about 1500. Suitable materials have viscosities of the order of about 500 mPa.s to about 200,000 mPa.s. The groups W of the polymeric material comprise at least partially of hydroxyl or hydrolysable groups selected, for example, from $-Si(R^2)_c(OH)_{3-c}$, $-SiR^2_d(OR^3)_{3-d}$ and $-Si(R^2)_2-R^4-SiR^2_k(OR^5)_{3-k}$ where R^2 is as aforesaid, and is preferably methyl or ethyl but most preferably methyl, R^4 is a divalent hydrocarbon group which may be interrupted by one or more siloxane spacers having up to six silicon atoms, each R^3 is an alkyl or oxyalkyl group in which the alkyl groups have up to 6 carbon atoms, each R^5 is an alkyl group having up to 6 carbon atoms; each of c , d and k have the value 0, 1 or 2. Preferably, R^4 is either a methylene or ethylene group, each R^3 and R^5 is independently a methyl or ethyl group, c is equal to 2 and d and k are equal to 0 or 1. Most preferably R^4 is an ethylene group, k is 0 and R^5 is an ethyl group. Other end groups which may optionally be present in addition to the hydroxyl or hydrolysable groups have the formula $-Si(R^2)_3$ wherein each R^2 is as previously described but is preferably a methyl group. Most preferred is a polydialkylsiloxane terminated with groups of the formula $-Si(CH_3)_2-(R^4)_2-Si(OR^5)_3$ where R^4 is a methylene or ethylene group.

- 7 -

[0013] The surface active filler (ii) is a reinforcing or semi-reinforcing filler and must be of a type which will be modified by the reaction with organosilane (iii). Preferably the surface active filler comprises a silica such as high surface area fumed silica, calcined silica and precipitated silica. One or more other finely divided, extending fillers such as crushed quartz, diatomaceous earths, barium sulphate, iron oxide, and carbon black may also be present in the composition. The proportion of such fillers employed will depend on the properties desired in the elastomer-forming composition and the cured elastomer. Usually the filler content of the composition will reside within the range from about 5 to about 150 parts by weight per 100 parts by weight of the polymeric material.

[0014] Organosilane (iii) is preferably present as a cross-linker. Organosilane cross-linkers are preferably selected from a silane having alkoxy, acetoxy, oximo, alkenyloxy or amino substituents. Most preferably the cross-linker is an alkoxysilane of the general formula

$R^2_{4-n}Si(OR^3)_n$ wherein R^2 and R^3 are as aforesaid and n has a value of 2, 3 or 4. Preferred organosilanes are those wherein R^2 represents an alkyl group having 1 to 6 carbon atoms for example methyl, ethyl, isopropyl or isobutyl or an alkenyl group such as vinyl, R^3 represents methyl or ethyl

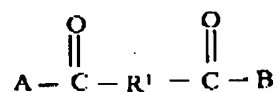
and n is 3. Examples of operative organosilanes are methyl trimethoxy silane, vinyl trimethoxy silane, methyl triethoxy silane, and vinyl triethoxy silane, isopropyl trimethoxy silane, propyl trimethoxy silane, phenyltrimethoxysilane, tetraethoxysilane and isobutyl trimethoxy silane. A

sufficient amount of this organosilane cross-linker is employed to ensure adequate stability of the composition during storage and adequate cross-linking of the composition when exposed to atmospheric moisture, however in the present application it is to be understood that a sufficient amount

- 8 -

of cross-linker must be present in order to form an in-situ modified filler.

[0015] The catalyst may be any suitable catalyst which accelerates the reaction process suitable catalysts are organic salts of metals such as titanium and zirconium tetra isopropyl titanate and tetra n butyl titanate and tetra tertiary butyl titanate. If a more rapid cure is desired, a chelate, for example a β -diketone or β -keto-ester, may be added to the mixture. Those β -diketone or β -keto-ester materials conventionally used as accelerators for titanium catalysts may be employed, for example ethyl aceto acetate and methyl aceto acetate. Alternatively the catalyst may comprise a mixture and/or reaction product of a compound (i) selected from $M[OR^6]_4$ and $M[OR']_b[Z]_z$ wherein M represents titanium or zirconium, each R^6 and R' is the same or different and is a primary, secondary or tertiary aliphatic hydrocarbon, and Z is a group of the formula -O-E-O- wherein E is an alkylene group comprising 1 to 6 carbon atoms or a branched alkylene radical comprising 1 to 6 carbon atoms and z is 0 or 2 in which case when b is 0, z is 2 and when b is 2, z is 1; and a compound (ii) of the general formula



25

wherein R^1 is selected from a methylene group or a substituted methylene radical having 1 to 6 carbon atoms,

30

A is selected from $-(CX_2)_rC(R^7)_3$ wherein r is from 0 to 5, and an adamantyl group or a derivative thereof;

- 9 -

B is selected from the group of $-(CX_2)_mC(R^7)_3$, wherein m is from 0 to 5;

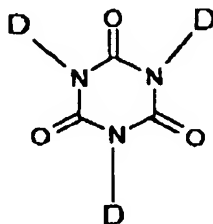
5 a monovalent alkyl group having from 1 to 6 carbon atoms and; OR^8 , wherein R^8 is selected from the group of $-(CX_2)_mC(R^7)_3$ and a monovalent alkyl group having from 1 to 6 carbon atoms;

10 wherein each X is the same or different and is selected from the group of a halogen radical and hydrogen, each R^7 is the same or different and is selected from the group of a halogen radical and an alkyl radical having one to eight carbon atoms, and when r is greater than 0 at least one of X or R^7 is a halogen radical as described in British patent
15 application No 0009684.2.

[0016] A further list of catalysts which may be used, include for example metal salts of carboxylic acids, such as lead octoate and dibutyltin dilaurate, dibutyltin diacetate, stannous octoate and chelated tin catalysts such as di(n-butyl)tin bis(ethylacetoacetate) and di(n-butyl) tin
20 bis(acetylacetonate). It is to be noted that these latter catalysts may alternatively be used as co-catalysts in combination with the titanate catalysts discussed above.

[0017] Preferred adhesion promoters include:-

25



- 10 -

wherein one D substituent is $-R_y-Si-(R''_x)(OR''_{3-x})$, in which R is a divalent hydrocarbon radical selected from alkylenearylene, alkylene, cycloalkylene and halo substituted derivatives thereof, R'' is an alkyl or haloalkyl radical with up to 8 carbon atoms, x is from 0 to 2 and y is 0 or 1, the remaining D substituents being selected from $-R_y-Si-(R''_x)(OR''_{3-x})$ as described above with the exception that x may be 0 to 3 or, styryl, vinyl, allyl, chloroallyl and cyclohexenyl, groups. Most preferably the adhesion promoter is a 1,3,5-tris(trimethoxysilylpropyl) isocyanurate

[0018] Other preferred adhesion promoters include aminoalkylalkoxy silanes, epoxyalkylalkoxy silanes, for example, 3-glycidoxypropyltrimethoxysilane and mercaptoalkylalkoxy silanes. Further preferred adhesion promoters are reaction products of epoxyalkylalkoxy silanes such as 3-glycidoxypropyltrimethoxysilane with amino-substituted alkoxysilanes such as 3-aminopropyltrimethoxysilane and optionally alkylalkoxy silanes such as methyltrimethoxysilane. The adhesion promoter used may alternatively be a mixture of any two or more any of the adhesion promoters listed above.

[0019] It will be noted that the adhesion promoters as disclosed above are of a reactive form in that given the opportunity they would normally interact with the surface active filler. The inventors believe that in previous processes when the adhesion promoter of this type was introduced prior to or concurrent with filler there would be an interaction during the mixing process between the adhesion promoter and the filler surface resulting in the "trapping" of a significant proportion of the adhesion promoter resulting in a significant reduction in the effectiveness of the adhesive properties of the resulting composition and by preventing this interaction from

- 11 -

occurring a composition with significantly improved adhesive properties results.

[0020] Another conventional ingredient which can be employed is a plasticiser. Plasticisers are introduced in order to reduce the modulus of the cured elastomer, a typical example of a plasticisers for this type of composition is a polydimethylsiloxane having terminal triorganosiloxy groups wherein the organic substituents are e.g. methyl, vinyl or phenyl or combinations of these groups. Such polydimethylsiloxanes normally have a viscosity of from about 5 to about 100,000 mPa.s at 25°C and can be employed in amounts up to about 80 parts per 100 parts by weight of the polymeric material.

[0021] Other additional ingredients may include pigments, water scavengers, which are typically the same compounds as those used as cross-linkers or silazanes and rheological additives for improving toolability of the composition. Examples include silicone organic co-polymers such as those described in EP0802233.

[0022] In a preferred composition there is present 35 to 90% by weight, and more preferably 45 to 55% by weight of polymer, 0 to 40% by weight and more preferably 30 to 40% by weight of a plasticiser, 0.5 to 5 % by weight and more preferably 1.5 to 3% by weight of catalyst, 0.5 to 5% by weight and more preferably 1.5 to 3% by weight of cross-linker, 6 to 20% by weight and more preferably 8 to 15% by weight of surface active filler, 0 to 5 % by weight and more preferably 1.5 to 2.5 % by weight of a rheological additive, 0.2 to 6% by weight and more preferably 0.8 to 3% by weight of one or more adhesion promoters and 0 to 3 % by weight and preferably 0.8 to 1.5% by weight of a fungicide.

[0023] As described above it is an essential step of the present invention to ensure that the mixture containing both

- 12 -

the organosilane cross-linker and filler is mixed for a period of time sufficient to enable the filler surface to be modified by the cross-linker. It is to be noted that other optional ingredients such as a water scavenger may also take part in this filler surface modification process when present in the composition. It is thought that the resulting production of an in-situ treated surface active filler enhances the adhesive effect of a subsequently introduced adhesion promoter as the adhesion promoter is substantially prevented from interaction with surface active filler.

[0024] Preferably the organosilane (iii) in the form of a cross-linker, catalyst (iv) and polymer (i) are mixed together prior to adding the filler. This premixing stage can take any form but it is particularly preferred to ensure that the catalyst and organosilane cross-linker are introduced into the mixture prior to the filler because addition of these components subsequent to the filler has a tendency to lead to slump problems in the resulting composition.

[0025] The organosilane cross-linker and catalyst are most preferably mixed together to form a premix prior to combination with the polymer and the polymer/premix mixture is thoroughly mixed prior to combination with the surface active filler.

[0026] The adhesion promoter may, for example, be added on its own, or in combination with an amount of any of the other ingredients other than the filler. Hence, the adhesion promoter may be added in combination with a rheology modifier and/or a fungicide or may alternatively may be added in combination with a proportion of the polymer, plasticiser, when present and a catalyst or co-catalyst.

- 13 -

[0027] In a batch type operation in accordance with the present invention there is provided a process comprising the steps of

5

a) loading polymer (i), organosilane(iii) and catalyst (iv) into an appropriate mixer and mixing thoroughly to form a blend;

10

b) adding the surface active filler (ii) into the blend ensuring that it is thoroughly dispersed for a predetermined period of time, such that after said predetermined time period the surface active filler (ii) contained in the mixture has been sufficiently modified by the organosilane(iii);

15

c) adding the or each adhesion promoter (v) and mixing until a final product is sufficiently homogeneous

20

d) devolatilising resulting mixture of step (b) and or the final product of step (c).

25

[0028] It is preferred that a plasticiser, particularly a polydimethylsiloxane having terminal trimethylsiloxy groups and a viscosity of about 100 mPa.s at 25°C, is introduced into the mixture concurrent with the polymer. Preferably the organosilane cross-linker and catalyst, optionally in combination with a water scavenger, are premixed prior to mixing with the polymer and optional plasticisers. In a preferred process a rheology modifier and/or fungicide may

30

- 14 -

be added into the composition at any stage of the mixing process.

[0029] Any appropriate continuous reactor suitable making compositions of the type described in the present invention may be utilised, providing the equipment enables the addition of an adhesion promoter subsequent to the cross-linker-surface active filler interaction.

[0030] Examples of continuous systems for the present invention include the continuous reactor described in EP0512730 which comprises a screw extruder having two mixing zones interlinked by an external residence zone. In a process in accordance with the present invention there is provided a continuous process utilising a screw extruder having two mixing zones interlinked by an external residence zone comprising the steps

- I. mixing polymer (i), catalyst (iv), organosilane (iii) in the first mixing zone prior to the introduction of surface active filler (ii),
- II. introducing surface active filler (ii) into the mixture resulting from step (I) in the first mixing zone and mixing until thoroughly dispersed, prior to entry onto the external residence zone such that the period of time in the external residence zone is utilised for the modification of the surface active filler and
- III. introducing one or more adhesion promoters (v) into the second mixing zone.

[0031] It is preferred that optional additives such as plasticisers and/or water scavengers are, when required, introduced in to the first mixing zone and are mixed prior to the introduction of surface active filler. The surface active filler is introduced into the first mixing zone such

- 15 -

that it is thoroughly dispersed into the mixture prior to reaching the external residence zone, such that the period of time in the residence zone is utilised for the modification of the surface active filler. By-products such as water are extracted in the second mixing zone. In such a system an input port may be introduced in the second mixing zone at an appropriate position such that the adhesion promoter can be introduced into the system at a point where it is homogenously mixed into the composition prior to packaging or alternatively an additional addition and mixing stage may be introduced after the second mixing zone for the introduction of the adhesion promoter.

[0032] A further alternative continuous process may utilise a continuous mixer of the type described in EP0739652 in this instance the process comprises supplying

- i. a premix of polymer (i), organosilane (iii) and catalyst (iv) and
- ii. a surface active filler (ii)

to a continuous mixing apparatus comprising a cylindrical body casing having a material feed opening at the top of said casing, a mixture discharge outlet at the bottom of said casing, a rotating disk within the casing, where the ratio of the diameter of the rotating disk (11) to the inside diameter of said casing is 0.80 to 0.95; an upper mixing compartment above said rotating disk and a lower mixing compartment below said rotating disk. The process comprises mixing said premix (1) with said surface active filler (II) in said upper mixing compartment by rotation of said disk to form a mixture, transferring said mixture into said lower mixing compartment and then adding one or more adhesion promoters prior to, subsequent to or concurrent with discharging said mixture through said discharge outlet.

[0033] Preferably subsequent to discharging the mixture, the mixture is de-aired in a de-airer and the adhesion

- 16 -

promoter (v) is introduced into the resulting mixture during passage of the mixture through the de-airer.

5 **[0034]** It is to be understood that the resulting product, for example a sealant, from any of the above processes in accordance with the invention provides significantly improved adhesion between sealant and a substrate such as glass or a window frame because substantially more of the adhesion promoter is available to react both within the product matrix and at the sealant/substrate interface
10 because there will be little or no interaction between the filler particles and the adhesion promoter because of the filler modification step in the process. Previous compositions not utilizing the process described herein resulted in final products containing a significant amount
15 of the adhesion promoter which had interacted with the filler. The efficiency of the adhesion promoters in sealants prepared in accordance with the method of the present invention is significantly improved compared with the prior art.

20 **[0035]** The resulting product is may be used as a sealant for glass, plastic, metals, wood, painted wood and the like.

25 **[0036]** A detailed description of one continuous process together with several examples of the invention are provided in the examples hereafter.

30 **[0037]** The invention will now be described by way of example and with reference to the accompanying drawings in which

Fig.1 is a plan view of a mixing apparatus utilised in the following examples

Fig.2 is a schematic drawing of the continuous mixing process utilised in the following examples to exemplify the process in accordance with the present invention.

- 17 -

[0038] In Figure 1 there is provided a continuous mixer (FUNKEN POWTECHS, INC - Japan) (100) having a mixer body (20) and a material feed section (30) for the mixer. A cylindrical body casing (1) forms the outer shell of mixer body (20), and a feed opening (2) receives a feed mixture that is provided at the centre of the upper plate (1a) of body casing (1). The lower part of the body casing forms an inclined surface (1b) having the shape of an inverted cone, and discharge outlet (3) is installed in said inclined surface (1b). A conical element (15) is provided at the centre of the casing bottom so as to form an annular V-shaped bottom with inclined surface (1b).

[0039] A cylindrical feed section casing (4) forms the outer shell of material feed section (30). Inlet (5) is connected at the side of feed section casing (4), and reservoir (6) is formed within feed section casing (4). An overflow tube (7) having the shape of an inverted cone is connected on the top of feed opening (2) on mixer body (20). This overflow tube (7) ascends substantially vertically and forms the inner wall of reservoir (6). The lower end of feed conduit (8) faces the inlet to overflow tube (7).

[0040] In the case of the present invention an organosilane cross-linker/catalyst/polymer mixture (SCP mixture) and optionally a plasticiser is fed into the material feed section (30) through inlet (5) while the surface active filler is introduced from feed conduit (8). The SCP mixture supplied by inlet (5) is first stored in reservoir (6), and then flows down the inner wall of overflow tube (7) from the top edge thereof. At this point, the surface active filler supplied through feed conduit (8) is mixed into said SCP mixture and the resulting surface active filler/SCP mixture descends into feed opening (2).

- 18 -

[0041] A rotating disk (11) is installed horizontally within the body casing (1) of mixer body (20) to face feed opening (2). This rotating disk (11) divides the casing interior into an upper mixing compartment (10), where a first-stage mixing operation is implemented, and a lower mixing compartment (12), where a second-stage mixing operation is implemented. The centre of rotation of this rotating disk (11) is fixed on the upper end of a rotating axle (16). Said rotating axle (16) is supported by a bearing element (16a) and extends to the exterior of casing (1). A pulley (17) is fixed at the bottom end of rotating axle (16), and the power for rotation is provided by an electric motor (not shown). The preferred range for rotation is from 400 to 3,000 rpm. An additive inlet (9) is provided in upper plate (1a), and additive inlet (9) opens into the upper mixing compartment (10) so that additives may be introduced into continuous mixer (100) concurrent with the addition of the filler/SCP mixture. The upper surface, outside edge, and lower surface of rotating disk (11) each carry two or more scrapers (13a), (13b) and (13c). Usually three of each type of scraper (13a), (13b) and (13c) are used but scrapers (13b) on the outer edge of rotating disk (11) may be omitted. Typically the mixture is mixed by a combination of the stirring action of rotating disk, or the stirring and scraping actions of these scrapers. Mixing proceeds as follows: the scrapers (13a) in the upper mixing compartment (10) scrape off the mixture adhering to the upper plate (1a); the scrapers (13b) scrape off the mixture adhering on the inner wall of the casing at the boundary between the upper mixing compartment (10) and the lower mixing compartment (12); and the scrapers (13c) in the lower mixing compartment (12) scrape off the mixture adhering on the inclined surface (1b) of the casing bottom.

- 19 -

[0042] The ratio of the diameter of the rotating disk (11) to the inside diameter of the cylindrical body casing (1) is particularly important to the quality of the dispersion of component (B), and values from 0.8 to 0.95, preferably from 0.85 to 0.9 are required herein. A ratio of less than 0.8 will produce deficient dispersion due to a "short pass" by the mixture and a ratio above 0.95 does produce dispersion, but does not permit transfer of the mixture into the lower mixing compartment (12).

10 [0043] The upper surface of rotating disk (11) may also comprise a large number of vertical mixing pins (14), which to further promote homogeneity. A conforming jacket may be provided for purposes of temperature control over the outer surface of the cylindrical body casing (1) of the mixer body
15 (20).

[0044] In the above apparatus, the surface active filler/SCP mixture entering the upper mixing compartment (10) from the feed opening (2) is subjected, while being radially transported outward on the rotating disk (11), to the first-stage mixing process based on stirring and scraping by the scrapers (13a) and mixing pins (14). The surface active filler/SCP mixture that has been mixed in the first-stage mixing process is then subjected to the second-stage mixing process based on shear between the circumference of the rotating disk (11) and the interior wall of the cylindrical body casing (1) combined with stirring and scraping by the scrapers (13b). The mixture that has been transported to the lower mixing compartment (12) then descends onto the inclined surface (1b) and is sheared while being scraped by
25 the ends of the scrapers (13c). The resulting additional dispersion of surface active filler induces a further lowering of the viscosity of the mixture. The mixture is then discharged through the discharge outlet (3).
30 Considerations of the quality of the dispersion make it

- 20 -

preferable for the filler/SCP/additive mixture in the lower mixing compartment (12) to reach a temperature from 120 to 150°C. Referring now to Fig 2 which provides a schematic view of a system for preparing organopolysiloxane compositions as described in the present invention. In figure 2 there are provided four main components, a mixer (101), continuous mixer (100), twin-screw de-airer (102) and cooler (99). The polymer, optional plasticiser, and a premix of catalyst and cross-linker are introduced into mixer (101) by way of supply lines 98, 97 and 96 respectively and are mixed together in mixer (101), before being fed to inlet 5 of continuous mixer (100). Surface active filler is introduced into mixer (100) through conduit (8). Prior to the present invention the adhesion promoter, for example, the reaction product of an aminoalkylalkoxysilane with an epoxyalkylalkoxysilane and optionally an alkylalkoxysilane and where required a silicone-glycol rheological additive were added into continuous mixer (100) by way of inlet 9, such that surface active filler, SCP mixture and adhesion promoter were introduced into the mixer at substantially the same time. These ingredients are mixed together due to the high rotation speed of the disk and the presence of mixing cams on it. The highest mixing shear is believed to occur between the mixer wall and the disk edge. The resulting mixture was continuously discharged from outlet (3) of the continuous mixer (100) and was then supplied to the feed inlet (95) of a vented twin-screw extruder 102 (L/D = 10) (DongSeo Machinery CO., Ltd -Korea) which is used as a de-airer. The water, volatiles, and air present in the mixture were continuously removed by the imposition of a vacuum within the vented twin-screw extruder through the vacuum vent opening (94). In addition an additive port (108) was provided for the introduction of a fungicide. The final product ejected from twin-screw de-airer (102), was

- 21 -

continuously discharged and transferred to a cooler (99) and was subsequently packaged in appropriate storage vessels.

[0045] In the present invention the addition of the adhesion promoter was not added at inlet (9) but was introduced into the lower region of continuous mixer (100) at an inlet port (110) as seen on Figure 2 or alternatively in combination with fungicide at inlet 108 in twin screw de-airer (102), the latter being preferred. The rheological additive is preferably still added through port (9) but may be added in combination with the adhesion promoter at inlet port (110) or inlet (108). Furthermore whilst inlet (108) is positioned prior to vacuum vent (94) in Figure 2 it is to be appreciated that the adhesion promoter may be introduced either prior to or after vent (94) in twin-screw de-airer (102). However it is to be understood that the following results indicate that the later the adhesion promoter is added the better the results providing appropriate mixing of the adhesion promoter is completed because the reaction between surface active filler and cross-linker has been given a greater length of time prior to the introduction of the adhesion promoter. The following examples further support this invention.

Example 1

25

[0046] This example was used to compare the adhesive characteristics of sealant compositions made on the continuous mixer (100) with adhesion promoter added from a variety of different inlets. Table 1 indicates the compositions used measured in parts by weight. The polymer was an ethyltriethoxysilyl terminated polydimethylsiloxane with a viscosity of 60000 mPa.s at 25°C (pol), the plasticiser was trimethylsilyl terminated polydimethylsiloxane with a viscosity of 100 mPa.s at 25°C

- 22 -

(plas). The catalyst used was a tetra tertiary butyl titanate (TtBT), the organosilane cross-linker was isobutyltrimethoxysilane (iBTMS), the surface active filler was CAB-O-SIL LM150 undensified fumed silica obtained from
5 Cabot, the rheological additive was a silicone-glycol indicated in Table 1 as RA1 the adhesion co-promoter AP1 was the reaction product of a γ -aminopropyltriethoxysilane, γ -glycidoxypropyltrimethoxysilane and methyltrimethoxysilane, the adhesion promoter AP 2 was a 1,3,5-
10 tris(trimethyloxysilylpropyl)-isocyanurate, Y11597 obtained from Witco and the fungicide was vinyzenc BP 5-5 PG 1000

- 23 -

Table 1 Formulations details.

Run	pol	Plas	TtBT	iBTMS	LM-150	RA1	AP1	AP2	Vinyzene
C1	50	34.5	2.2	2.2	12.0	2.00	0.0	0.0	0.3
C2	50	34.5	2.2	2.2	12.0	2.00	0.8	0.0	0.3
C3	50	34.5	2.2	2.2	12.0	2.00	0.8	0.4	0.3
4	50	34.5	2.2	2.2	12.0	2.00	0.8	0.4	0.3
5	50	34.5	2.2	2.2	12.0	2.00	0.8	0.4	0.3
6	50	34.5	2.2	2.2	12.0	2.00	0.8	0.4	0.3
7	50	34.5	2.2	2.2	12.0	2.00	0.8	0.4	0.3

[0047] Run C1, C2 and C3 are all comparative runs wherein in C1 no adhesion promoters were used in the composition, in C2 only adhesion promoter AP1 was added through inlet 9 and in C3 a mixture of AP2 and AP1 was added through inlet 9 and hence concurrent with the other ingredients. Runs 4,5,6 and 7 are exemplary of the invention in that in run 4 AP 1 and AP2 were both introduced into continuous mixer (100) through inlet (110) in run 5 the AP1 and AP2 were introduced into the reaction mixture in combination with fungicide at inlet (108) on twin screw de-airer (102). Run 6 used AP1 introduced at inlet 9 and AP2 was added after de-airing by mixing in a Drais mixer and run 7 had both AP1 and AP2 added in a Drais mixer subsequent to the mixing process described above. Adhesion tests were undertaken using the products obtained by the above processes. Adhesion was measured on a variety of substrate samples treated with the compositions and cured for 1 week at room temperature (dry cure) or for 1 week at room temperature and one week of water immersion (dry/wet cure). Prior to application the substrates were cleaned with an isopropanol/acetone mixture. Adhesion was assessed using the bead test (CTM 1007) whereby subsequent

- 24 -

to curing the beads were pulled at 90° and the failure was rated as follows:

0: adhesive failure - poor adhesion)

1: boundary or mixed mode (adhesive/cohesive) failure
5 acceptable adhesion.

2: cohesive failure - excellent adhesion

[0048] The plastics adhesion data presented in table 2 are the average results for dry wet curing obtained on different substrates, namely: 4 polymethylmethacrylate
10 (PMMA) samples (obtained from ROHM&HAAS, ICI and ATOCHEM);
10 unplasticised polyvinyl chloride samples (obtained from KOMMERLING, REHAU, SALAMANDER, VEKA, LG, KCC, SOLVIN and, ALUPLAST); 7 polyester coated aluminium (PCA) samples
15 (obtained from DUPONT, AKZO-NOBEL) and 2 polyvinylidene fluoride coated aluminum samples.

Table 2 Plastics adhesion data

Dry/Wet average on several substrates)

Run	PMMA	UPVC	PCA	PVF2
	4 dry/wet	10 dry/wet	7 dry/wet	2 dry/wet
C1	0.0	0.0	0.1	0.0
C2	1.3	0.1	0.3	0.0
C3	1.4	0.3	0.6	0.0
4	1.6	0.5	0.6	0.0
5	1.4	1.7	1.1	0.3
6	1.3	0.8	0.7	0.0
7	1.1	1.3	0.9	0.3

[0049] As expected, the Run C1 shows very poor plastics
20 adhesion due to the absence of any specific silane adhesion promoter. PMMA adhesion develops to a satisfactory and quite constant level as soon as AP1 is added and is not significantly effected by the presence of AP2. However

- 25 -

adhesion to the other substrates is enhanced by the presence of AP2 and the best results are obtained when AP1 and AP2 are introduced into the mixture in de-aired (102).

5 Example 2

[0050] Additional adhesion trials were carried out on samples prepared by way of Runs 5 and 6 described above, on various uPVCs from KOMMERLING, REHAU (2 types), SALAMANDER, 10 VEKA (3 types), LG, KCC, SOLVIN, ALUPLAST, BASF, VINIDUR (2 types) showing perfect dry adhesion. After water immersion, 100% cohesive failure was achieved with the samples from KOMMERLING, REHAU, VEKA, LG, KCC, SOLVIN, ALUPLAST. The adhesion performance was superior to Durasil® W15-2000, a 15 commercially available sealant (Dow Corning), particularly after water immersion. Run 5a used a white sealant which was identical with the composition made for run 5 but which had a titanium dioxide pigment paste added when the resulting product was being packaged into cartridges.

20

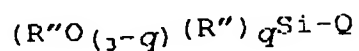
Table 3 uPVC adhesion data: dry/wet average: FJM#C".

Run	colour	uPVC window frame	
		Average ALL	
		RT	H2O
W15-2000	clear	1.6	1.0
Run 6	clear	1.7	1.2
Run 5	clear	1.7	1.4
Run 5a	white	1.7	1.2

- 26 -

CLAIMS

- 1) A process for making an organopolysiloxane composition comprising mixing the following components
- i) a polymer having not less than two groups bonded to silicon which are hydroxyl or hydrolysable groups or a partial condensate thereof,
 - ii) a surface active filler selected from silica, titania, zinc oxide, clay, mica and precipitated calcium carbonate
 - iii) an organosilane comprising at least two silicon bonded reactive groups which are reactable with said surface active filler
 - iv) a catalyst and
 - v) an adhesion promoter having at least one hydrolysable group, having the formula

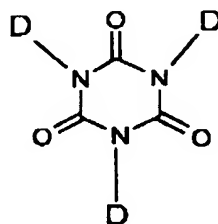


wherein R'' is as defined above, Q is a saturated, unsaturated or aromatic hydrocarbon radical functionalised by a group selected from amino, mercapto, ether, epoxy, isocyanato, cyano, isocyanurate acryloxy and acyloxy and mixtures thereof and q is 0 to 3, characterised in that organosilane (iii) is mixed with surface active filler (ii) to form an in-situ modified surface active filler prior to the introduction of the adhesion promoter.

- 2) A process in accordance with claim 1 wherein the organosilane (iii) is a cross-linker.

- 27 -

- 3) A process in accordance with claim 1 or 2 wherein the polymer is an organopolysiloxane having polydiorganosiloxane chains according to the general formula $-(R^2SiO)_t-$ in which each R^2 represents a methyl group or ethyl group and t has a value from about 200 to about 1500 said organopolysiloxane being terminated by at least one group selected from $-Si(R^2)_c(OH)_{3-c}$, $-SiR^2_d(OR^3)_{3-d}$ and $-Si(R^2)_2-R^4-SiR^2_k(OR^5)_{3-k}$ where R^4 is a divalent hydrocarbon group which may be interrupted by one or more siloxane spacers having up to six silicon atoms, R^3 is an alkyl or oxyalkyl group in which the alkyl groups have up to 6 carbon atoms, R^5 is an alkyl group having up to 6 carbon atoms; each of c , d and k have the value 0, 1 or 2.
- 4) A process in accordance with any preceding claim wherein organosilane (iii) is an alkoxy silane selected from methyl trimethoxy silane, vinyl trimethoxy silane, methyl triethoxy silane, and vinyl triethoxy silane, isopropyl trimethoxy silane, propyl trimethoxy silane, phenyltrimethoxysilane, tetraethoxysilane and isobutyl trimethoxy silane.
- 5) A process in accordance with any preceding claim wherein the adhesion promoter comprises at least one compound of the formula



- 28 -

wherein one D substituent is $-R_y-Si-(R''_x)(OR''_{3-x})$, in which R is selected from alkylenearylene, alkylene, cycloalkylene and halo substituted derivatives thereof, R'' is an alkyl or haloalkyl radical with up to 8 carbon atoms, x is from 0 to 2 and y is 0 or 1, the remaining D substituents being selected from $-R_y-Si-(R''_x)(OR''_{3-x})$ wherein x is 0 to 3 or, styryl, vinyl, allyl, chloroallyl and cyclohexenyl, groups.

- 6) A process in accordance with any one of claims 1 to 4 wherein the adhesion promoter comprises a 1,3,5-tris(trimethoxysilylpropyl) isocyanurate and/or a compound selected from an aminoalkylalkoxy silane, an epoxyalkylalkoxy silane, a mercaptoalkylalkoxy silane, or a reaction product of an epoxyalkylalkoxy silane with an amino-substituted alkoxy silane and an alkylalkoxysilane.
- 7) A process in accordance with any preceding claim wherein the organosilane (iii), catalyst (iv) and polymer (i) are mixed together prior to adding the filler (ii).
- 8) A batch process in accordance with the process of any preceding claim comprising the steps of
 - a) loading polymer (i), organosilane (iii) and catalyst (iv) into an appropriate mixer and mixing thoroughly to form a blend;
 - b) adding the surface active filler (ii) into the blend ensuring that it is thoroughly dispersed for a predetermined period of time, such that after said predetermined time period the surface active filler (ii) contained in the mixture has

- 29 -

been sufficiently modified by the organosilane (iii);

- c) adding the or each adhesion promoter (v) and mixing until a final product is sufficiently homogeneous
- d) devolatilising resulting mixture of step (b) and or the final product of step (c).

9) A continuous process in accordance with the process of any one of claims 1 to 7 utilising a screw extruder having two mixing zones interlinked by an external residence zone comprising the steps:-

- I. mixing polymer (i), catalyst (iv), organosilane (iii) in the first mixing zone prior to the introduction of surface active filler (ii),
- II. introducing surface active filler (ii) into the mixture resulting from step (I) in the first mixing zone and mixing until thoroughly dispersed, prior to entry onto the external residence zone such that the period of time in the external residence zone is utilised for the modification of the surface active filler and
- III. introducing one or more adhesion promoters (v) into the second mixing zone.

10) A continuous process in accordance with any one of claims 1 to 7 comprising supplying

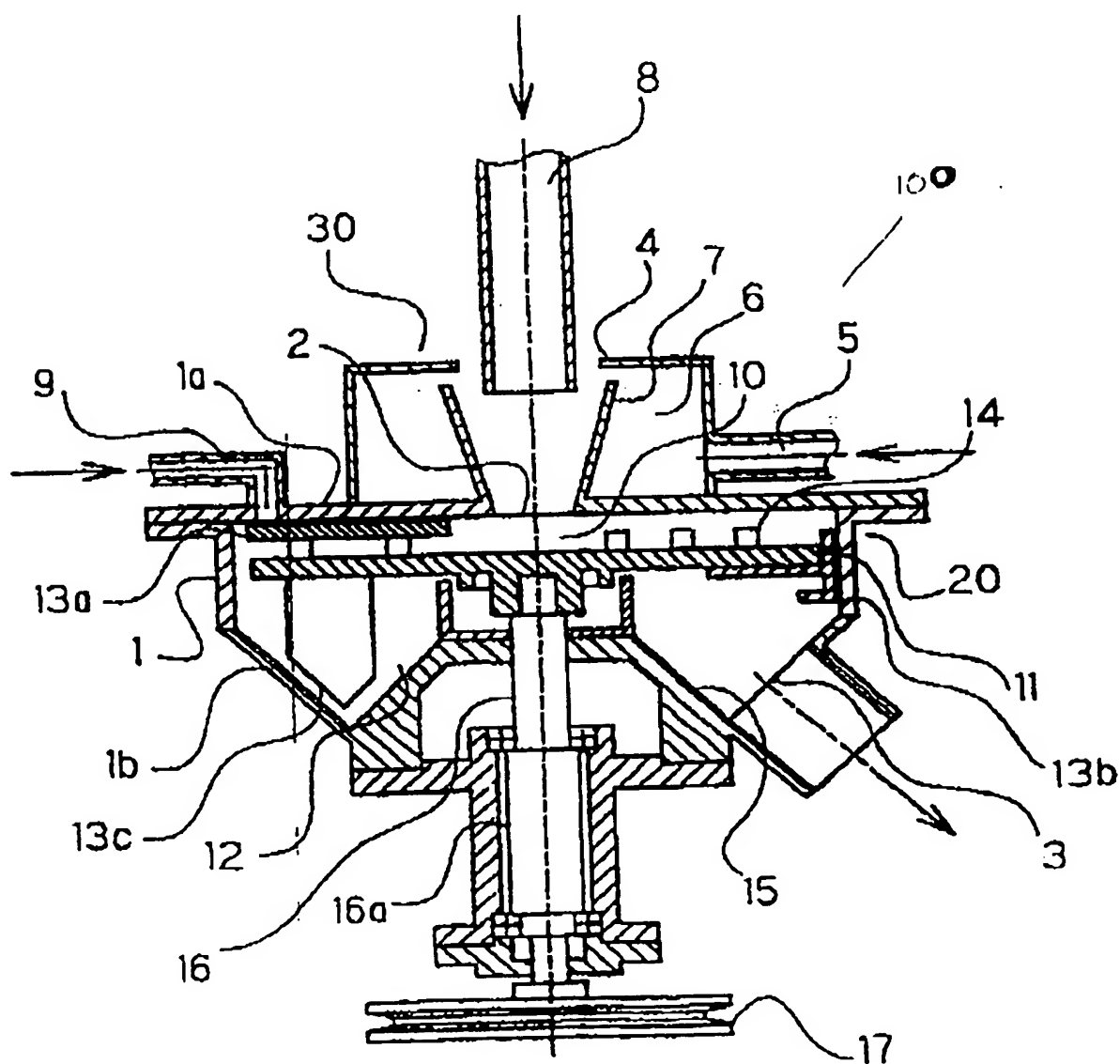
- i. a premix of polymer (i), organosilane (iii) and catalyst (iv) and
- ii a surface active filler (ii) to a continuous mixing apparatus comprising a cylindrical body casing (1,1a, 1b) having a

- 30 -

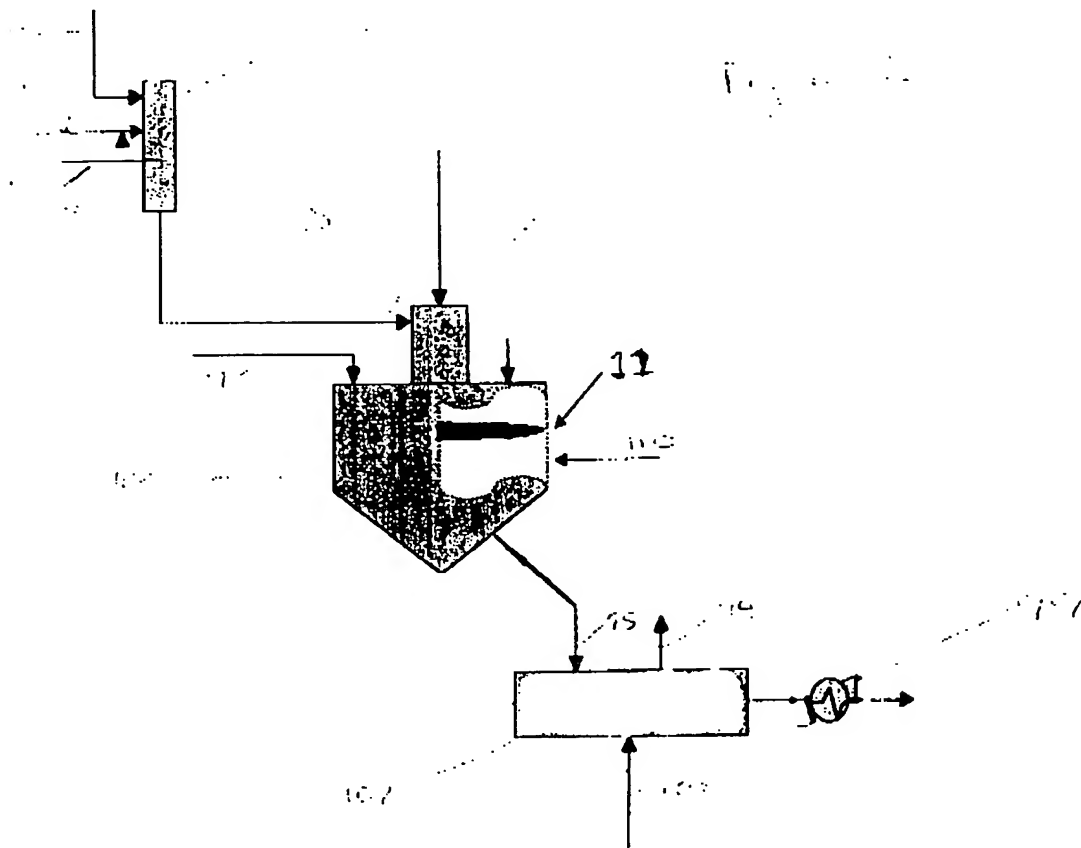
material feed opening at the top of said casing (8,14,9), a mixture discharge outlet (3) at the bottom of said casing (1,1a, 1b), a rotating disk (11) within the casing (1,1a, 1b), where the ratio of the diameter of the rotating disk (11) to the inside diameter of said casing is 0.80 to 0.95; and an upper mixing compartment (10) above said rotating disk (11) and a lower mixing compartment (12) below said rotating disk; and mixing said premix (I) with said surface active filler (II) in said upper mixing compartment (10) by rotation of said disk (11) to form a mixture, transferring said mixture into said lower mixing compartment (12) and then adding one or more adhesion promoters (v) prior to, subsequent to or concurrent with discharging said mixture through said discharge outlet (3).

- 11) A continuous process in accordance with claim 10 wherein subsequent to discharging the mixture, the mixture is de-aired in a de-airer (102) and the adhesion promoter (v) is introduced into the mixture during passage of the mixture through the de-airer (102).
- 12) An organopolysiloxane composition obtainable from any process in accordance with claims 1 to 11.
13. A sealant comprising the composition of claim 12.
14. Use of a composition in accordance with claim 12 as a sealant.

Figure 1.









1950